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► **To cite this version:**

Maxime Deutsch, Nicolas Claiser, Mohamed Souhassou, Béatrice Gillon. Joint Refinement of Charge and Spin Densities. 9th International Conference on Polarised Neutrons in Condensed Matter Investigations, Jul 2012, Paris, France. pp.10 - 17, 10.1016/j.phpro.2013.03.169 . hal-01522044

**HAL Id: hal-01522044**

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Submitted on 12 May 2017

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9<sup>th</sup> International Workshop on Polarised Neutrons in Condensed Matter Investigations  
(PNCMI2012)

## Joint refinement of charge and spin densities

Maxime Deutsch<sup>abc\*</sup>, Nicolas Claiser<sup>ab</sup>, Mohamed Souhassou<sup>ab</sup> and Béatrice Gillon<sup>c\*</sup>

<sup>a</sup>Université de Lorraine, Laboratoire de Cristallographie, Résonance Magnétique et Modélisations BP 70239, F54506 Vandoeuvre-lès-Nancy France

<sup>b</sup>CNRS Laboratoire de Cristallographie, Résonance Magnétique et Modélisations, UMR 7036 Vandoeuvre-lès-Nancy, F-54506 France.

<sup>c</sup>Laboratoire Léon Brillouin (CEA-CNRS, UMR 12), Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette, France.

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### Abstract

A new charge and spin density model and the corresponding refinement software were recently developed to combine X-ray and polarized neutron diffraction experiments [1]. This joint refinement procedure allows getting access to both charge and spin density distributions by refining both spin up and down parameters for magnetic atoms. The paper is focused on the refinement procedure and its application to the case of an end-to-end azido double bridged copper(II) complex. The results of this joint refinement of X-ray and polarized neutron diffraction data are presented.

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Selection and peer-review under responsibility of the Organizing Committee of the 9th International Workshop on Polarised Neutrons in Condensed Matter Investigations

Keywords: Joint refinement; Charge density; Spin density; Molecular magnetism; End-to-end azido bridge

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### 1. Introduction

Interaction between crystals and X-ray/polarized neutrons, is due to all/unpaired electrons and allows describing and modelling the charge and spin density [2, 3]. Models have been developed for each single experiment: charge density modelling for X-ray diffraction (XRD), spin density modelling for polarized neutron diffraction (PND)... and few attempts have been made to combine several experiments in order to

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\* Corresponding author. E-mail address: [maxime.deutsch@cea.fr](mailto:maxime.deutsch@cea.fr)

have a more general and thorough electron density modelling. The very first X/N joint structure refinement on the basis of X-ray and unpolarized neutron diffraction (UND) was proposed by Duckworth et al in 1969 [4] and authors at that time already noted that with a joint refinement "it is shown that a more satisfactory refinement is obtained than by analysing each set of data independently". P. Coppens et al [5] were among the first, in 1981, to propose a joint X-ray/neutron refinement in order to limit the effects of correlation between structural and charge density parameters. The weighting schemes have been discussed in Coppens paper but are not of primary importance because the numbers of neutron and X-ray diffraction data were similar (2315 for X ray and 1912 for neutrons).

A procedure of joint charge and spin density refinement on XRD and PND data was first proposed by Becker and Coppens [6] using the Hansen & Coppens multipole model [7] for the paired electron density and a molecular orbital model for the unpaired electron density. However applications of this method to experimental data for transition metal complexes were not successful [8].

This paper reports on the results of a joint refinement procedure recently developed [1] and is divided in two parts. The first part will present the general feature of a joint X-rays, neutron and polarized neutrons refinement and the second part will show the preliminary results on an end-to-end Azido Double Bridged Cu<sup>II</sup> di nuclear complex (Cu<sub>2</sub>L<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>) (L=1,1,1-trifluoro-7-(dimethylamino)-4-methyl-5-aza-3-hepten-2-onato) complex.

## 2. Joint X-ray and polarized neutron refinement: Methodology and strategy

Charge and spin density distributions can be obtained separately from XRD and PND data respectively using the Hansen & Coppens multipolar model [7]. As charge and spin densities are described by a similar multipolar atom centred model with a common parameterization, it enables for a combined treatment of the two quantities. A joint refinement of the spin and charge densities in an extended model which distinguishes the up and down spin contributions, is then possible. With this new model we have to distinguish two types of atoms: non-magnetic atoms, which are refined with a classical Hansen & Coppens model and atoms carrying a spin magnetic moment, for which the parameters are split. For magnetic atoms, the valence ( $P_v$ ), multipolar ( $P_{lm\pm}$ ) populations and expansion/contraction parameters ( $\kappa, \kappa'$ ) may be split in up and down counterparts. The extended model is thus described as:

$$\rho(\mathbf{r}) = \rho_{core}(r) + P_v^\uparrow \kappa^{\uparrow 3} \rho_v^\uparrow(\kappa^\uparrow \mathbf{r}) + P_v^\downarrow \kappa^{\downarrow 3} \rho_v^\downarrow(\kappa^\downarrow \mathbf{r}) + \sum_{l=0}^{l_{max}} \kappa'^{\uparrow 3} R_l(\kappa'^\uparrow r) \sum_{m=0}^l P_{lm\pm}^\uparrow y_{lm\pm}(\theta, \phi) + \sum_{l=0}^{l_{max}} \kappa'^{\downarrow 3} R_l(\kappa'^\downarrow r) \sum_{m=0}^l P_{lm\pm}^\downarrow y_{lm\pm}(\theta, \phi)$$

where  $\uparrow$  and  $\downarrow$  state for spin up and down parameters.  $\kappa^\uparrow / \kappa^\downarrow$  were introduced because the spin up and spin down electron distributions may not have the same radial extension [6] therefore the refinement against XRD and PND data leads to a simultaneous determination of spin and charge density distributions.

The spin density is the difference between spin up and spin down densities:

$$s(\mathbf{r}) = P_v^\uparrow \kappa^{\uparrow 3} \rho_v^\uparrow(\kappa^\uparrow \mathbf{r}) - P_v^\downarrow \kappa^{\downarrow 3} \rho_v^\downarrow(\kappa^\downarrow \mathbf{r}) + \sum_{l=0}^{l_{\max}} \kappa^{\uparrow 3} R_l(\kappa^\uparrow r) \sum_{m=0}^l P_{lm\pm}^\uparrow y_{lm\pm}(\theta, \phi) - \sum_{l=0}^{l_{\max}} \kappa^{\downarrow 3} R_l(\kappa^\downarrow r) \sum_{m=0}^l P_{lm\pm}^\downarrow y_{lm\pm}(\theta, \phi)$$

Several assumptions have to be done to carry out such a refinement gathering X-ray (XRD), unpolarized neutron (UND) and polarized neutron diffraction data (PND):

- The cell parameters are those obtained from the X-ray experiments (generally more precise due to the larger number of measured reflections).
- Two sets of anisotropic atomic displacement parameters  $U_{ij}$  and extinction parameters are refined from X-ray and neutron separately due to the possible difference of crystal size or difference in the temperatures of the data collections.
- The electroneutrality (all X-rays monopoles) and number of unpaired electrons (spin monopoles) constraints are added using Hamilton method [9].

One of the major concerns in the joint refinement strategy is the weighting scheme: indeed we deal with a complete XRD data set to very high or high resolution compared to medium resolution and incomplete PND data set therefore the weights have to be carefully assigned.

Three weighting schemes were introduced in order to manage these differences:

- UNIT, where the score function  $C$  minimises the sum of the  $\chi^2$  of each experiment; this model was used in the joint refinement (UND and XRD) by Coppens and co-workers [5]:

$$C(\chi_j^2(x)) = \sum_j \chi_j^2(x)$$

where  $j$  stands for an experiment (XRD, UND, or PND) and

$$\chi_j^2(x) = \sum_i |F_i^{jO} - F_i^{jC}(x)|^2 / \sigma^2(F_i^{jO})$$

where  $i$  runs over all the measured structure factors  $F_o$ ;  $F_c$  are the calculated ones and  $\sigma^2$  is the estimated variances of  $F_o$ .

- NLOG for which the score function  $C$  is defined as:

$$C(\chi_j^2(x)) = \sum_j N_j \log(\chi_j^2(x))$$

where  $N_j$  is the number of observation of data set  $j$

This scheme was proposed by Bell et al [10] and Gillet et al [11a] [11b] based on the logarithm of  $\chi^2$  to reduce the weighting ratio between large and small data sets and hence to better take into account the contribution of the small data set.

- LOG: a new weighting scheme proposed, independent from the data set size, where the score function is:

$$C(\chi_j^2(x)) = \sum_j \log(\chi_j^2(x))$$

This last weighting scheme should favour the small data set by giving approximately the same weight for the small and the big data sets.

Because of the large difference between the numbers of reflections for each experiment (~10000 for XRD and several hundreds for PND), the NLOG or LOG scheme may prevent from neglecting the experiments with small size data collections.

The initial model for the joint refinement is the density model obtained by X-ray multipolar refinement only. For atoms supposed to carry a spin density, their valence and multipole populations are split into up and down and refined against all data sets.

### 3. Charge and spin density of an end-to-end azido double bridged Cu<sup>II</sup> di nuclear complex (Cu<sub>2</sub>L<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>).

#### 3.1. Description of the structure and charge density

The crystal structure, with the P2<sub>1</sub>/n space group, may be described by discrete neutral centrosymmetric five coordinated dinuclear dimers (Cu...Cu = 5.068(1) Å) [12]. The azido groups bridge in an asymmetric fashion (Cu-N<sub>3</sub> = 2.000(1) Å; Cu-N<sub>5</sub> (azido) = 2.346(1) Å) (figure 1).

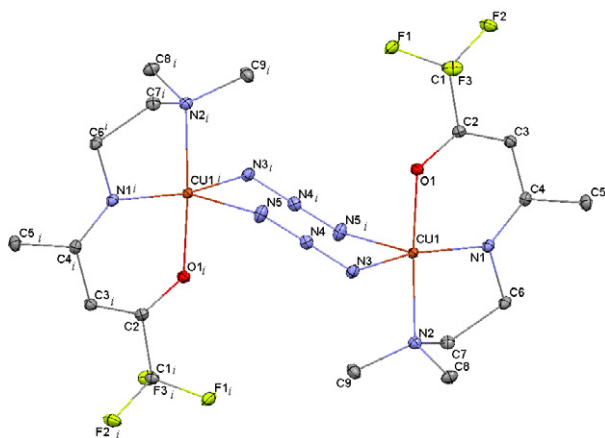


Figure 1. Ortep view of Cu<sub>2</sub>L<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> structure at 10K. The ellipsoids show 50% probability surfaces. A set of 72,709 reflections was collected at 10K on an Oxford Diffraction SuperNova single-crystal diffractometer with Mo K $\alpha$  radiation which were reduced to 15,731 independent reflections using SORTAV ( $R_{\text{all}} = 0.042$ ). The conventional multipole refinement converged to  $R_w(F) = 1.51\%$  for 7208 reflections with  $I/\sigma > 3$  and  $\sin(\theta/\lambda) < 1.0 \text{ \AA}^{-1}$ .

Figure 2(a) presents the O1-Cu-N1 plane of the static deformation charge density map, which is the difference between the final multipolar model and the spherical density described by neutral spherical atoms model. The bonding density shows up as expected in the ligand interatomic bonds and nitrogen lone pairs; the  $d_{x^2-y^2}$  orbital of copper is depleted whereas  $d_{xy}$  is populated. The oxygen and nitrogen lone pairs face the copper d orbital depletions ( $d_{x^2-y^2}$ ), as expected from the ligand field theory.

### 3.2. Experimental spin density modeled from PND only

A previous PND study of the induced spin density at 2K under a field of 5T was reported by Aronica *et al.* [12]. The usual PND data treatment for centric space groups was applied, i.e. the magnetic structure factors were deduced from the experimental flipping ratios using the  $F_N$  values calculated from the neutron structure determined at 30K.

The correction for hydrogen nuclear spin polarization was applied. To take into account the orbital contribution using the dipolar approximation, a first monopole population  $P_v$  for  $\text{Cu}^{2+}$  with magnetic form factor ( $\langle j_0 \rangle + \langle j_2 \rangle$ ) was refined. Therefore the  $P_{00}$  population of the monopole (with spherical form factor  $\langle j_0 \rangle$ ) corresponds to the pure spin contribution to the magnetization density (see ref. [15]).

In first approximation, for the joint refinement, as the orbital contribution represent only a 10% correction it will be neglected (we consider the Cu atom quenched).

(For more details about the PND data treatment see Lecomte et al 2011 [13]).

**Table 1.** Model parameters (monopole populations in  $\mu_B$ ) and agreement factors.

	3d orbital model	Charge and spin joint refinement
Contraction coefficients	$\kappa'_{\text{Cu}}$ 1.46(6)	
Cu1 monopole 1 ( $P_v$ )	0.071(6)	0.78(3)
monopole 2 ( $P_{00}$ )	0.715(6)	
O1 monopole	0.046(4)	0.04(6)
N1 monopole	0.045(5)	0.05(4)
N2 monopole	0.080(5)	0.07(4)
N3 monopole	0.030(5)	0.02(4)
N4 monopole	0.004(5)	0.01(4)
N5 monopole	0.031(7)	0.03(4)
sum	1.02(2)	1.00
N obs	212	212
N param	13	34
GOF	1.30	1.37
$R_w( 1-R )$	0.079	0.078

The large  $\kappa'$  value (Table 1) indicates that the atomic spin density on Cu is more contracted than expected from literature [14]. The sum of the monopole populations, equal to  $1.02(2) \mu_B$  per asymmetrical unit, provides a value of  $2.04(4) \mu_B/\text{mol}$  for the total induced moment due to spin and orbital contributions. This value is in very good agreement with the experimental magnetization of  $1.98 \mu_B/\text{mol}$  from SQUID measurements at 2K under 5 Tesla [12].

The section map of the spin density in the  $\text{CuO}_1\text{N}_1$  (x,y) plane is represented in Figure 3(a).

### 3.3. Joint refinement

The joint refinement was performed by splitting the charge density model (for magnetic atoms) in  $\rho\uparrow$  and  $\rho\downarrow$ . This initial charge density model is obtained by the X-ray multipole refinement described above. The joint refinement gives very close results to those obtained by the separated studies in terms of statistical agreement factors (Table 1):  $R_w(F)_X=1.52\%$  compared to  $1.51\%$ , and  $R_w(1-R)_{NP}=7.8\%$  compared to  $7.9\%$  and in terms of spin and charge distribution. As shown on figures 2 and 3 the static deformation density maps and the spin density maps compare very well with the previous separated studies. The oxygen and nitrogen lone pairs face the copper charge depletions, while a cross shape spin density directed towards ligand atoms, which is interpreted as spin delocalization, is observed. Moreover values of the magnetic momentum on each atom also compare very well (Table 1) despite larger standard deviations values due to the real determination of  $\rho\uparrow$  and  $\rho\downarrow$ . Indeed with the joint refinement we determine  $\rho\uparrow$  and  $\rho\downarrow$  with  $\sigma(\rho\uparrow)$  and  $\sigma(\rho\downarrow)$  and if the standard deviation on the total density (determined by X-rays) is only several percent of the monopole it represents the major uncertainty on these two values.

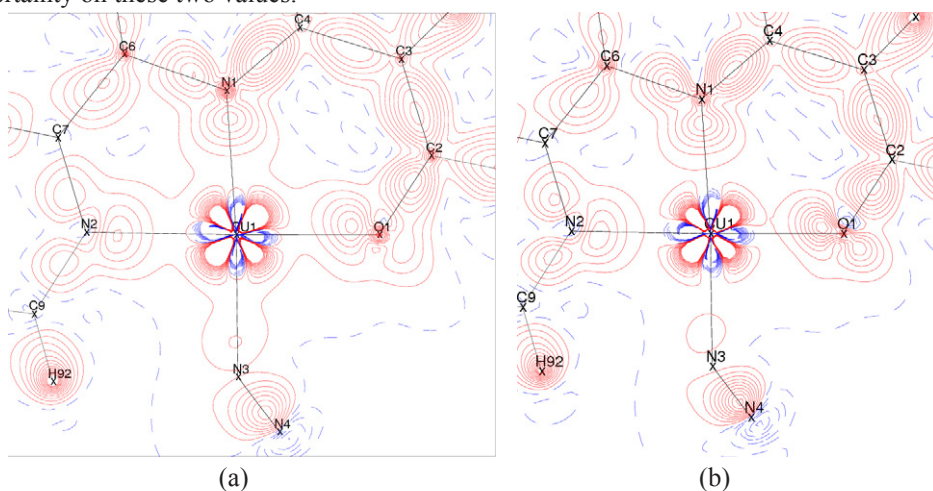


Figure 2. Static deformation density (a) obtained with X-rays data refinement only and (b) obtained with a joint refinement (b). Contours  $0.1 \text{ e} \cdot \text{\AA}^{-3}$

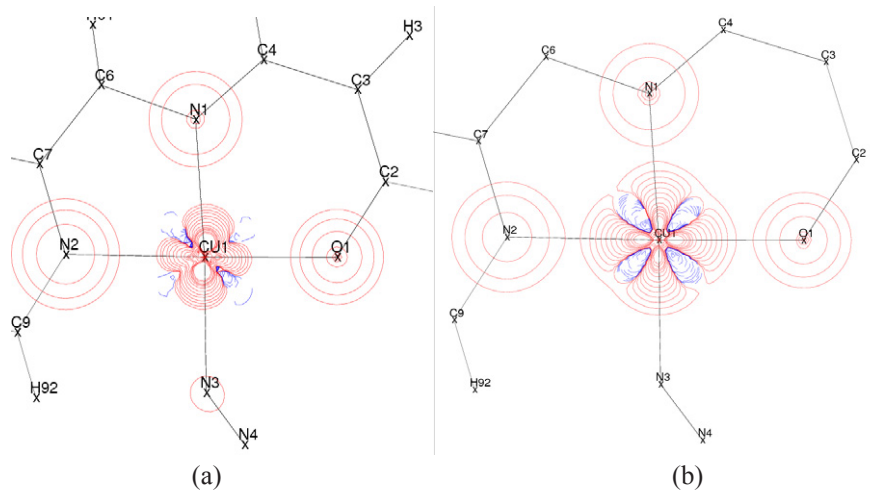


Figure 3. Representation of spin density maps obtained with PND data refinement only (a) and the obtained with a joint refinement (b). contours drawn for  $\pm 0.01 * 2^n e. \text{\AA}^{-3}$  ( $n=0,9$ ), plus contours  $\pm 2, \pm 3, \pm 4 \mu_B. \text{\AA}^{-3}$  Red line: positive, blue dashed line: negative.

#### 4. Conclusion

The new joint refinement procedure of XRD and PND data gives us access to charge and spin densities simultaneously. It also allows a more detailed refinement of spin density thanks to XRD data that gives the global shape of the total charge density and then constraints several spin parameters without initial assumption.

#### Acknowledgements

This work has been supported by l'Agence Nationale de la Recherche (CEDA Project) and M.D. thanks C.N.R.S for PhD fellowship.

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